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NEW YORK UNIVERSITY
Physics Department, Washington Square

FINAL REPORT

on

LUMINESCENCE, INFRARED RESPONSE AND ENERGY STORAGE OF
VARIOUS LUMINESCENT MATERIALS IN RELATION TO
PREPARATIVE METHODS AND CONDITIONS

Submitted to:

U.S. Army Research Office (Durham)
Box CM, Duke Station
Durham, North Carolina

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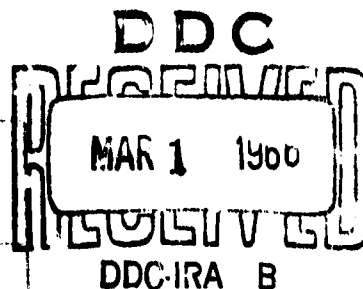
Grant No. DA-ARO(D)-31-124-G420

October 1, 1964 to 31 January 1965

December, 1965

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FINAL REPORT

Radiation and Solid State Laboratory
Physics Department
New York University
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AROD Project No. 3987-P

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PREPARATIVE METHODS AND CONDITIONS

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Submitted by:

Herbert Kallmann

H. Kallmann
Professor of Physics
Laboratory Director

December, 1965

PART I. TRAPPING AND INFRARED RESPONSE OF A "BLUE-GREEN" ZNS PHOSPHOR[☆]

I. Introduction

The investigation of the trapping processes and infrared response of ZnS phosphors has been the subject of many investigations.^(1,2,3,4,5)

Two main bands of infrared giving rise to quenching and stimulation of luminescence and photoconductivity have been found for ZnS phosphors prepared under different conditions and with various activators; one at about 0.7μ , the other at 1.3μ . Because of the similar response of quenching and stimulation, it has been proposed⁽⁶⁾ that the ionized activator (trapped hole) is mainly responsible for the IR absorption and forms a coupled system with the trapped electron. Following IR absorption it gives rise to quenching, stimulation, conductivity, or the energy is dissipated by transfer to the lattice. Besides these relatively shallow trap levels there may also exist deeper trap levels due to special impurities such as Cr and Cu. Electrons trapped in these levels behave completely different from those in the above described shallower levels. The holes are still localized at ionized activators forming uncompensated Cu^{++} , but the electrons trapped in these special centers are released by IR into the conduction band and then trapped by the shallower levels connected with the activators. Heating can reverse this process; the electrons leave the shallow traps and are retrapped by the deep centers.⁽⁷⁾

[☆] This paper was given at the International Symposium on Luminescence, Munich, 1965.

To further investigate the mechanism of trapping and infrared response, we have studied these effects with a special ZnS Cu activated phosphor showing the reversible blue-green transformation.⁽⁸⁾

II. Phosphor and Apparatus

(a) The phosphor was made by offering a non-activated, non-luminescent ZnS powder Cu, and Cl, and by firing it at 1150°C in an H_2S atmosphere. Upon cooling, its normal luminescence is blue with the main emission peak at 4500\AA and a smaller component at 5200\AA . If the phosphor is heated to 400°C and cooled rapidly the emission changes to green (5300\AA) with a blue component of about 20%, thus showing the typical blue-green shift.

(b) Measurements are performed with the sample mounted on a brass plate and covered by a conductive coated glass plate and placed in a Hofman dewar with three ports; one for the uv excitation (3660\AA), one for infrared irradiation (Bausch and Lomb monochromator), and one for viewing with an RCA 1P21 photomultiplier. The temperature could be varied between liquid nitrogen and $+200^{\circ}\text{C}$. Glow curves were made at a heating rate of $12^{\circ}\text{C}/\text{minute}$.

(c) Photoconductivity measurements were made using AC impedance techniques. A general radio 716-C bridge with an oscillator and detector were used at 1000 cps.

III. Experimental Results and Discussions

(a) Glow Curve Measurements

The phosphor was excited with ultraviolet light at liquid nitrogen temperature (LNT) until the luminescence reached an equilibrium. Since very little trap release occurs at these temperatures and since the glow area does not increase when the uv intensity is increased beyond a certain level, it is assumed that all traps are filled. After the uv was turned off, the glow curve was taken for both phases of this phosphor. They are shown in figures 1 and 2 as curves a. As can be observed, they are very similar to the green phase, but shifted only slightly deeper trap levels (higher temperatures). By comparing this glow area to a phosphor previously investigated⁽⁷⁾, one concludes that this sample has $\sim 10^{18}$ shallow traps/cm³, which is the same order of magnitude as the incorporated copper.

Glow curves were taken after these phosphors were quenched (de-excited) and irradiated at low temperatures, but with a shorter irradiation time so that the luminescence reaches only about 25% of the equilibrium level. These are shown in figures 1 and 2 as curves b. It is seen from the comparison of these curves that the reduction of excitation decreases the glow curve strongly, but that the shape of the glow curve is not changed, and the glow maxima occur at the same temperature in both phosphors. This result is in contradiction to the idea that when traps are not filled to saturation, electrons evaporate from shallower traps into the conductivity band and are retrapped by deeper traps during

the glow curve, as is the case with the above-mentioned phosphors⁽⁷⁾ which contain deeper trap levels. This is not the case in these phosphors. Experiments with other phosphors which also do not contain special trapping centers gave similar results.

One could explain the results by the assumption that heating does not remove the electrons into conductivity band from which they can be retrapped but to special emission levels, from which they can radiatively return directly to the ground state. In order to test this possibility, simultaneous conductivity measurements were made (using AC impedance techniques) and these measurements (see dotted line, curves 1c and 2c), show that during heating the conductivity of the sample is considerably increased. Thus, there is no doubt that heating releases a considerable portion of the electrons into the conductivity band. One must thus look for another explanation for the fact that the shape of the glow curve remains unchanged when only partially excited.

There is the possibility that the width of the glow curve is caused by some interaction with the lattice and that in reality the electrons released at different temperatures are not really released from traps of different depths. The following experiment shows that one really deals with levels of different properties. After the phosphor has been excited at LNT, infrared of 1.2μ was applied, and a new glow curve was taken. The shape of the glow curve is now found to be changed (figures 1 and 2, curve d). The low temperature portions of the glow curve has been drastically diminished, whereas the portion between -100° and 0° has been hardly changed. This means that the electrons released in this temperature range are bound in different levels than those released at a

Lower temperature, since they respond to 1.2μ radiation quite differently. Shorter wavelength of IR have an effect on the deep traps too, but empty the more shallow ones preferentially. Even at temperatures higher than -180° the electrons in the deeper levels are not very strongly affected by IR.

These experiments show that the electrons are bound in different levels but that the electrons are not retrapped in the deeper levels when these are partially empty. One can explain this by the assumption already suggested from other arguments, namely that the electrons freed in this temperature range are trapped only in the neighborhood of ionized activators. If there are less ionized activators there are less trap levels of this type available. Thus under incomplete excitation, practically all the available traps of this type are occupied so that no shift from lower levels to unoccupied deeper levels can occur since there are not much deeper traps from which electrons are released only at a temperature above 0°C has not yet been established.

(b) Effects of infrared

The quenching of the luminescence when infrared is added to uv excitation is shown in figures 3 and 4; for the blue phase, there are two quenching maxima, one at $\sim 0.7\mu$, and the other at $\sim 1.3\mu$, and these maxima occur at both room temperature and liquid nitrogen temperature. In the green phase, these two maxima are observed only at room temperature; at LNT there is no quenching with IR wavelength greater than 1.1μ .

The IR induced stimulation (light flash when IR is added to uv excitation) of these phosphors, however, is quite different from the behavior of most ZnS:CuCl phosphors. First, there is a very strong maximum of stimulation peaking sharply at an IR wavelength of 1.2μ . For the blue phase, the peak amplitude is 52 times greater than the fluorescent light level; this enhancement is unusually high. The green phase does not show such a large flash, but the curve of stimulation versus IR wavelength is the same for both phases.

There is another peculiarity for this "blue-green" phosphor. For most ZnS phosphors the maximum of stimulation coincides roughly with the maximum of quenching. This is not the case here. Figure 3 shows clearly that the maximum of the stimulation occurs at the point of minimum quenching. This could be interpreted to mean that the stimulation and quenching processes are based on different elementary processes.

In order to test this point we have measured the quenching effect of infrared on the succeeding glow curves rather than on the equilibrium luminescence. This is done by illuminating the phosphor at LNT with uv and after excitation, adding infrared of various wavelengths, and thereafter determining the glow area. The result is shown in curves d in figures 3 and 4 for both phases of this phosphor. The shape of the quenching of the glow area as a function of IR wavelength of these phosphors is now seen to be similar to the normal quenching response curve for other phosphors. Thus, the infrared quenching response of both phases of these phosphors is almost identical and is also very similar to the response curves of other ZnS:CuCl phosphors.

In the previous section, it was seen that the application of infrared light of 1.2μ decreases the shallow traps but did not diminish deeper traps, as seen in the subsequent glow curves. In agreement with this it is found that only the shallowest traps are responsible for the strong stimulation observed with 1.2μ IR. After excitation at LNT, and a dark interval of seven minutes, IR of 1.2μ is applied. The experiment is then repeated with the difference that during the dark interval the phosphor is heated to a certain temperature (T) and a portion of the glow area is removed. Then the phosphor is recooled to LNT and IR applied again. The stimulation as a function of the size of the removed glow area is given in Table I; it is seen that the stimulation decreases strongly as the low temperature portion of the glow area is decreased. Thus, it is these shallowest levels which give rise to the strong stimulation. When the removed glow area, the area of the stimulation peak, and the remaining glow area are added and compared to the total glow area without IR applied, a quenching of the total emission is observed which becomes weaker with larger removed glow areas.

The conclusion that the stimulation peak depends mostly on electrons in shallow traps is further borne out by the observation that the stimulation decreases when the dark interval between termination of activation at LNT and IR application is lengthened, and that this decrease is strongest during the first 15 minutes, but slows down very considerably for longer dark periods at LNT.

The IR stimulation was also checked during a glow curve at

intermediate temperatures when deeper traps are still filled but the shallower traps are already emptied. At temperatures above -100°C , there was no stimulation and only a small decrease in the succeeding glow area. This is different from the results obtained⁽⁹⁾ with a normal ZnS:CuCl green phosphor where the stimulation flashes were found to be proportional to the instantaneous glow emission and thus to the number of electrons left in these deeper levels. If one goes to higher temperature, there is quenching of luminescence but still not stimulation.

Infrared also influenced the ratio of the blue to green emission during the glow. In the blue phase of the phosphor the blue portion is about 10 times larger than the green portion during the glow. This ratio is drastically changed by IR. In figure 5, the spectral glow curves are shown for the blue phase with and without a 10 minute period of irradiation by IR (1.2μ) at LNT immediately before the glow curve is taken. The curves are normalized to the same maximum value for blue and green but the blue emission is about 10 times greater than the green. As can be seen, it is the blue portion which is considerably reduced by IR (compare curve a to b, and c to d); the total area is reduced by a factor of about 10 with the maximum shifted from -128°C to -95°C . For the green portion the area is decreased only in the low temperature region, and the shift is negligible. This holds true for the phosphor in its green phase as well.

These results as well as the results described in figures 1 and 2,

and the stimulation curves in figures 3 and 4 also show directly that the green component is considerably less affected by IR of longer wavelengths than the blue component. This again indicates that the electrons in these trap levels are closely connected to activators which are responsible for the blue emission.

(c) Deep Traps

As discussed in section IIIa, the glow curve does not extend very noticeably above 0°C . This might lead one to conclude that this phosphor contains no deep trap levels for electrons. Results given below show that this is not so; there are considerable numbers of very deep traps present, which, however, are not detectable in the glow up to 150° .

A very large deficiency area is obtained at room temperature with both phases of the phosphor. This RT deficiency area is one-third as large as the deficiency area obtained at LNT (see below), and since the latter is due to both deep and shallow traps, this indicates that the number of deep traps ($> 0^{\circ}\text{C}$) is approximately one-half the number of shallow levels. Thus, one has in this phosphor about $5 \times 10^{17}/\text{cm}^3$ deep traps and $10^{18}/\text{cm}^3$ shallow traps.

In experiment No. 1 of Table II the phosphor was completely quenched (heated in the dark to $+150^{\circ}\text{C}$), then cooled to LNT and irradiated with uv. The deficiency area obtained (11,000 in arbitrary units), corresponds to the total number of traps, deep and shallow; experiment No. 2 obtained at RT after thorough quenching gives the deficiency area due to deep traps (3400). In experiment No. 3 the

phosphor is excited at RT until all the deep traps are filled, then cooled to LNT and excited. The deficiency area now obtained (7900) should give the number of shallow traps that had to be filled; this figure is close to the difference between the two previous areas obtained.

In experiment No. 4, the quenched phosphor was excited at LNT until a deficiency area of 3400 units (roughly $1/3$ the normal LNT deficiency area) was obtained. It is then heated to RT at which temperature a rise curve is obtained. During this heating interval, a glow area of 900 units is observed. If all traps were filled to one-third of their saturation value during the excitation, the deficiency area expected at RT would be approximately 2200 without retrapping. Since it was 1500, one concludes that a portion of the electrons released from shallow traps during the low temperature glow were retrapped in the deep levels or that no retrapping at all occurred and the electrons are more easily trapped in the deep traps than in the shallow traps during the excitation process. We cannot discriminate between these possibilities.

The decay of the RT deficiency area at room temperature was measured and found to be very slow, even after 24 hours the deficiency area upon reirradiation was only a small portion of that of the quenched phosphor. This means that these electrons are bound in relatively deep levels. That the release of these electrons is not observed in the glow area at higher temperature can be understood as follows: The luminescent efficiency of this phosphor decreases very strongly at about 150°C due to the release of holes. Apparently the

electrons are bound in deeper levels than the holes, so that the latter are already released by thermal action while the electrons are still trapped. Thus one has radiationless recombination of free holes with trapped electrons. The nature of these deep trap levels is not yet ascertained.

IV. Conclusions

(1) The fact that the low temperature portion of the glow curve has a similar shape (and peaks at the same temperature) regardless of the duration of excitation (when the high temperature traps are filled) can be explained if one assumes that the levels giving rise to this part of the glow curve are created only when an activator is ionized, so that every electron trapped in these shallow levels is in the neighborhood of a positively charged activator. When an electron is released by thermal action at low temperature, it cannot be retrapped in deeper levels of the same range because practically no unoccupied levels of this type exist for any state of excitation. This is true for both phases of this phosphor and for other phosphors as well.

When infrared is added after excitation, the succeeding glow curves show a marked shift to higher temperatures. Infrared from 0.7μ to 1.3μ thus appears to be more effective in emptying the shallower levels. This shows that the levels of this temperature range are physically distinguishable from each other.

(2) The large stimulation observed with the blue phase of the phosphor, peaking at 1.2μ is due to the release of electrons from very shallow levels. This is shown by the observation that after stimulation,

the low-temperature part of the glow curve is strongly reduced while the remainder is unaffected. This cannot be due to retrapping as seen from the experiments done with various durations of excitation. Another indication that only the shallowest levels give rise to this stimulation is that if the experiment is performed at a slightly elevated temperature (shallow levels almost empty), the stimulation is strongly decreased.

(3) Deficiency area measurements indicate a considerable number of deep traps (approximately half the number of shallow traps) which cannot be observed in glow curve measurements. This is explained by the fact that these levels are so deep that the high temperatures required for their release lie in a temperature range of very low luminescent efficiency.

These deep traps may also be coupled to ionized activators, since they do not play a large role in retrapping electrons freed from the shallow range.

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Table I

| <u>Removed Portion of the Glow Area (arbit. units)</u> | <u>Amplitude of Stimulation Peak (arbit. units)</u> |
|------------------------------------------------------------|---------------------------------------------------------|
| 0 | 23 |
| 240 | 4.7 |
| 390 | 1.5 |
| 900 | 0.15 |

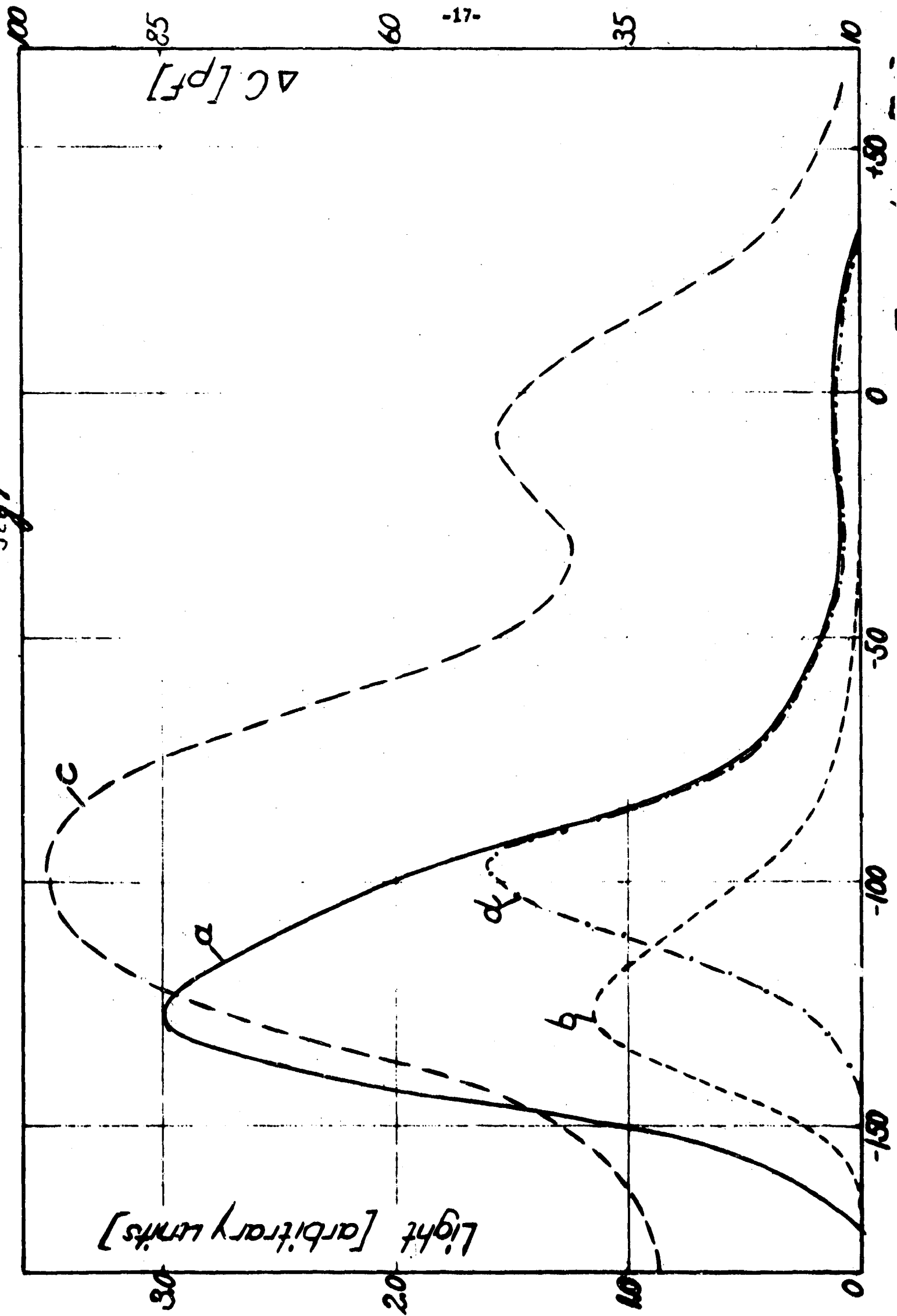
Table II

| <u>Excitation</u> <u>TEMP</u> | | <u>Deficiency Area</u> <u>(arbit. units)</u> | | |
|----------------------------------|-----------------|-------------------------------------------------|--------------|--------|
| <u>TEMP</u> | <u>DURATION</u> | <u>AT TEMP</u> | <u>VALUE</u> | |
| No. 1 | LNT | till equilibrium | LNT | 11,000 |
| No. 2 | RT | till equilibrium | RT | 3,400 |
| No. 3 | RT | till equilibrium | LNT | 7,900 |
| No. 4 | LNT | till 1/3 equilibrium | RT | 1,500 |

FIGURES

- Fig. 1 -** Glow curves of the blue phase. a - glow curve after full excitation, b - after partial excitation, c - C glow curve, d - glow curve after 10 minutes IR 1.2μ .
- Fig. 2 -** Glow curves of the green phase. a - glow curve after full excitation, b - after partial excitation, c - C glow curve, d - glow curve after 10 minutes IR 1.2μ .
- Fig. 3 -** Stimulation and quenching of the blue phase. a - stimulation at LNT, b - quenching at LNT, c - quenching at RT, d - quenching of the glow curve.
- Fig. 4 -** Stimulation and quenching of the green phase. a - stimulation at LNT, b - quenching at LNT, c - quenching at RT, d - quenching of the glow curve.
- Fig. 5 -** Spectral glow curves of the blue phase. a - blue part of the glow curve, b - blue part after IR 1.2μ , c - green part of the glow curve, d - green part after IR 1.2μ .

Fig 1



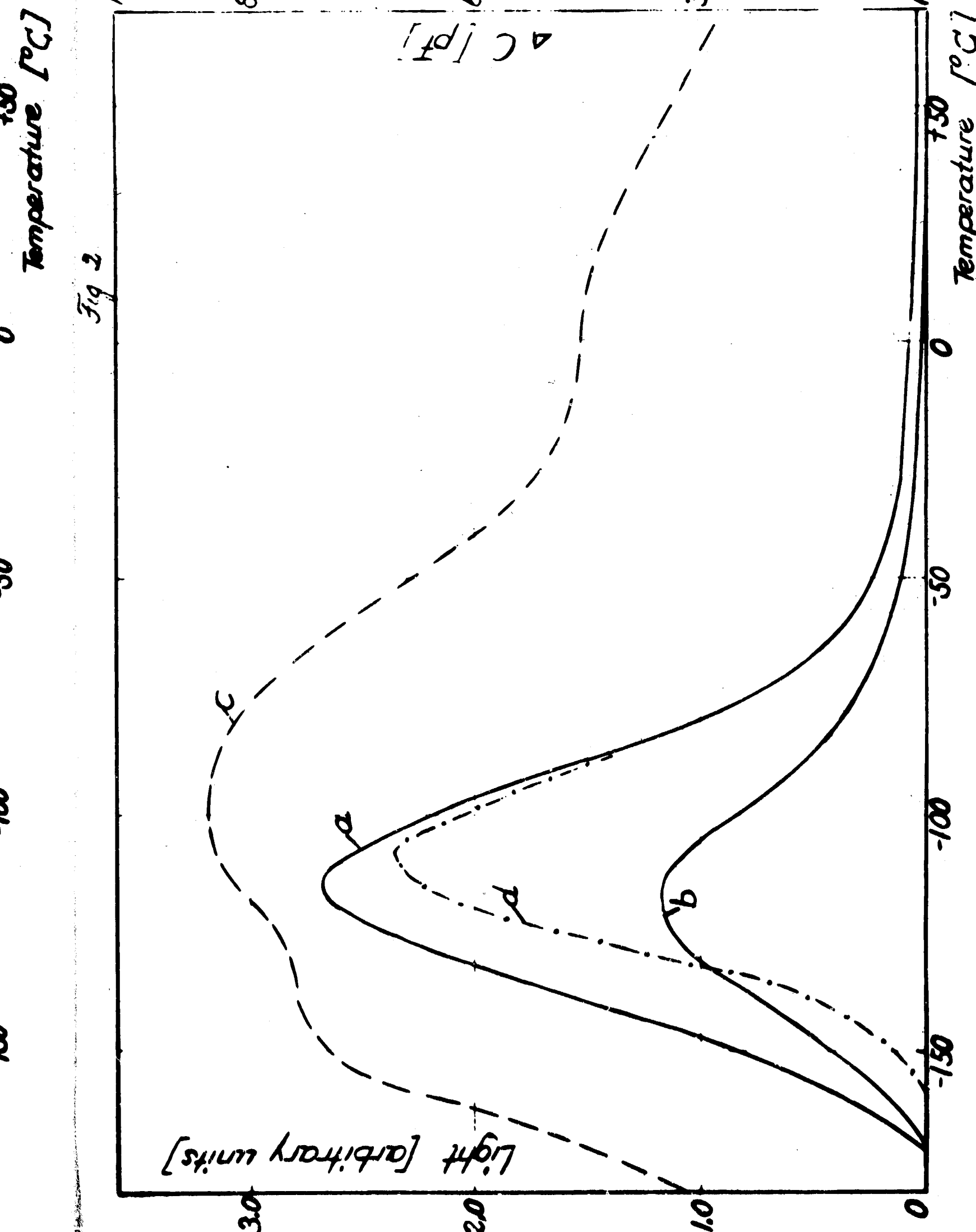


Fig 3

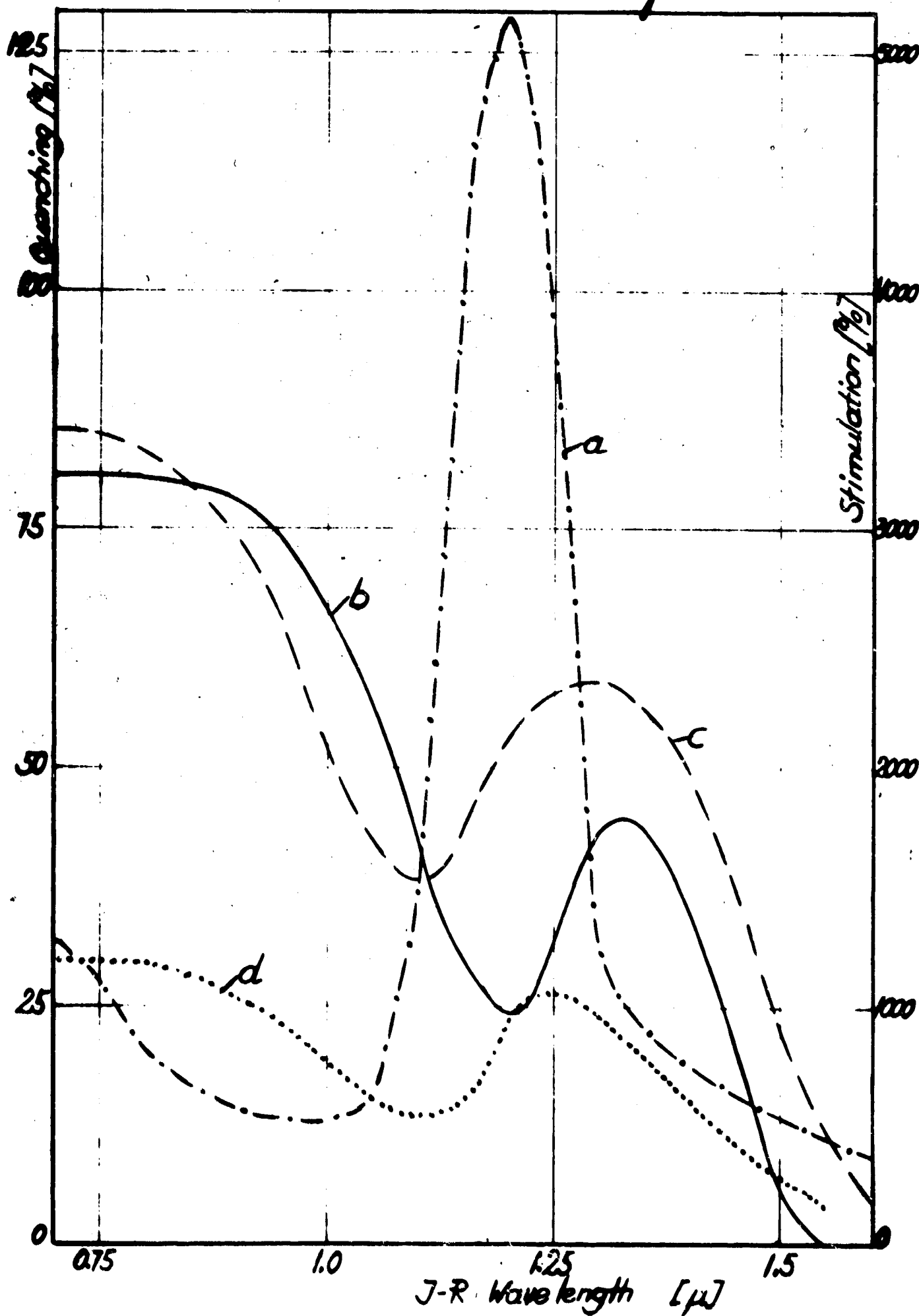
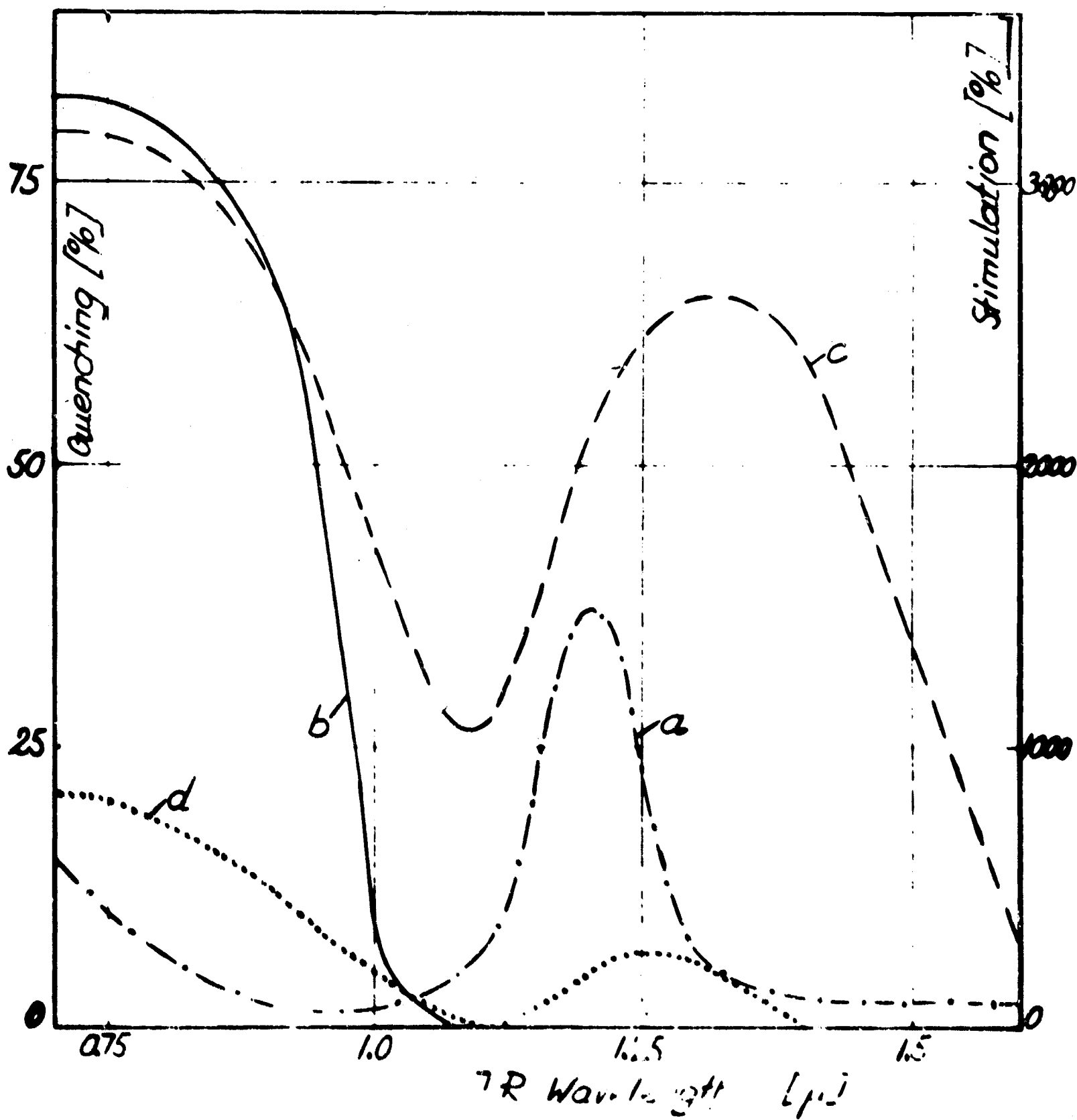


Fig. 4



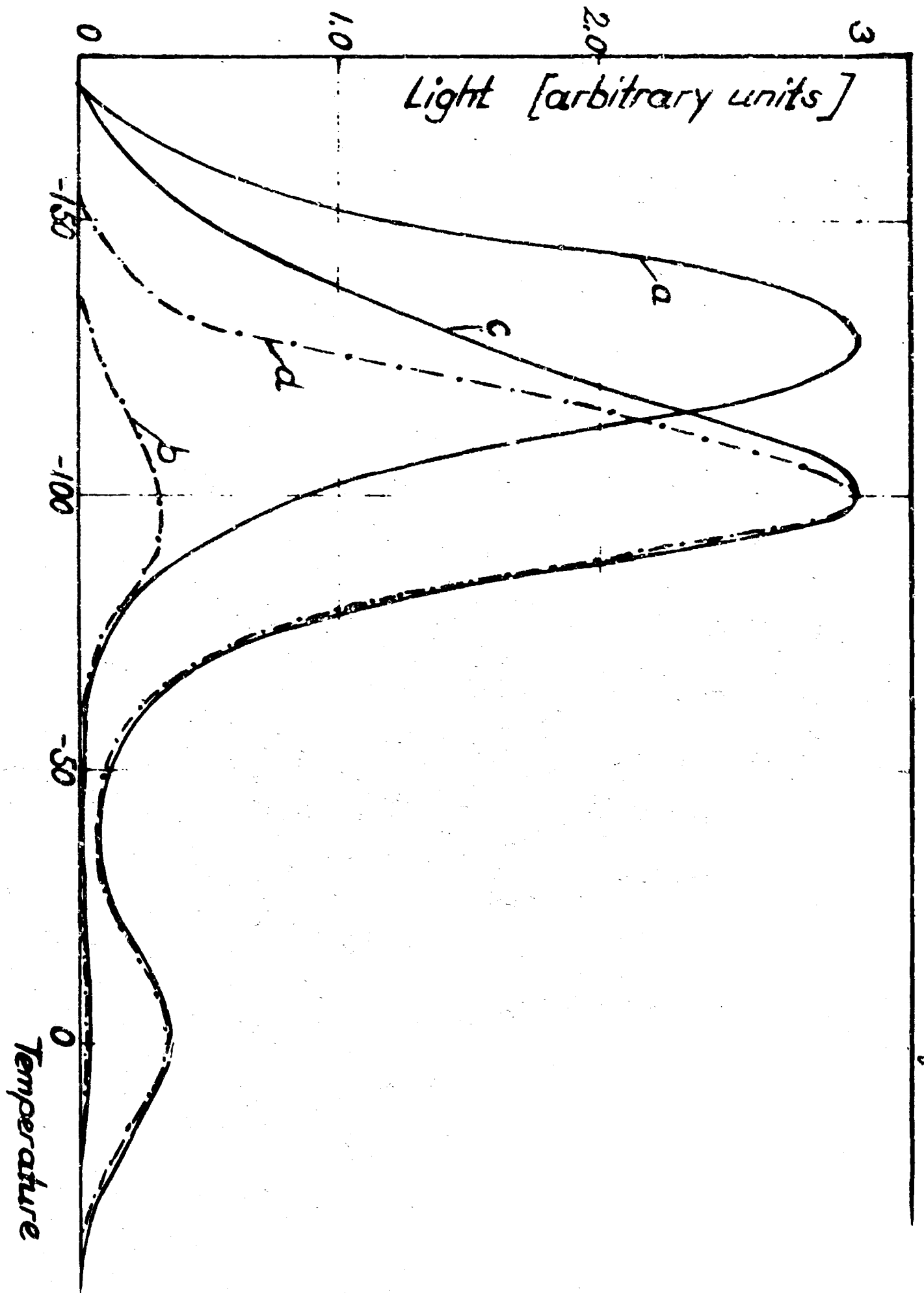


Fig. 6

Part II. Photovoltaic Effects Observed With Thin Films of Zinc Sulfide[☆]

Introduction

In 1957 Pensak reported a photovoltaic effect of exceptionally high voltage obtained with films of cadmium telluride.¹ Kallmann et al, have observed an analogous effect with silicon and germanium layers.² Trester has reported similar results with germanium.³ Ellis et al⁴, Merz⁵, Cheroff and Keller⁶ as well as Lempicki⁷ have observed this effect with zinc sulfide crystals. The mechanism of this effect has not been completely elucidated.

Results

This note reports on observations of photovoltages along the surface of thin films of zinc sulfide deposited on a Pyrex support. The samples used have a film thickness of several microns; the dimensions of the support are about 1 cm x 2 cm. The principal observations are as follows:

(a) Samples made from a ZnS:Cl (self-activated) phosphor showed photovoltages of up to several hundred volts when evaporated at an angle.

Samples made from ZnS:CuCl and from non-activated ZnS showed almost no effect.

(b) The photovoltage depends markedly on the angle of evaporation.

In a given set of films prepared simultaneously (Table 1), the photovoltage at room temperature increases with increasing angle of evaporation for a given light intensity. Under tungsten illumination of 130mw/cm^2 ,

[☆] This paper will be submitted for publication.

the photovoltage is almost zero for a zero evaporation angle and may exceed 200 volts at 40° , the maximum angle used. In this table, V_E is the voltage measured by an electrometer (input resistance 10^{11} ohms); V_o is the open circuit voltage obtained by using a compensating circuit, and R is the dark resistance of the sample.

(c) Under illumination, the side of the sample which is nearer to the evaporation source becomes positive with respect to the more distant. This indicates that electrons diffuse toward the support during excitation, possibly because of a faster recombination rate in this region.

(d) The polarity of the photovoltage remains the same, regardless of whether the film is illuminated directly or through the support. This behavior agrees with the observations of Trester on germanium films³; some of the silicon layers investigated showed a change in polarity.²

(e) This photovoltage is largest with samples of very high resistance ($\sim 10^{13} \Omega$) in the dark and under illumination. However, it is still noticeable with samples whose resistance is about 10^{11} ohms.

(f) Table 2 gives results with tungsten illumination ($\lambda >$ absorption edge) of various intensities for the 40° sample of Table 1. V_E and V_o are obtained as above; from these two the effective internal resistance of the sample is obtained (last column). Over the range of intensities given here, the photovoltage is proportional to the intensity, but the resistance remains constant. The resistance of the sample in the dark is $\sim 2 \times 10^{14}$ ohms, about 4 times greater than the values obtained under tungsten illumination.

(g) In Table 3, the results of tungsten illumination, UV illumination, and the super position of the two on another sample are compared with each other. In all cases, the radiation was incident on the open surface of the sample.

The UV source emits wavelengths on either side of the absorption edge, but only the energy on the short wavelength side is strongly absorbed and it produces a much higher excitation as evidenced by the strongly decreased photoresistance upon the UV application. In spite of this higher photoresponse, the photovoltage is smaller; thus the short wavelength UV excitation produces smaller photovoltages than weakly absorbed light although it produces larger photocurrents.

When UV is added to tungsten light it is seen that the additional UV reduces the photovoltage produced by tungsten light alone. V_0 is reduced by 90% and the corresponding resistance by more than 99%.

Conclusions

The following model would explain the results observed. It does not require involved assumptions regarding crystal structure as postulated by Neumark⁸ in an explanation of large photovoltages in quasi-monocrystals.

We assume that the layer consists of small ZnS monocrystals which are separated from each other by ZnS material which does not consist of a single crystal but is of more complicated structure. A drawing of this arrangement is shown in Fig. 1. The regularly arranged monocrystals are lined up in the direction of the evaporator, and each displays a

photovoltage because the recombination rate at the surface of the support is larger than that at the upper surface. In this way a concentration gradient (probably of electrons) develops, resulting in a voltage of $\frac{kT}{e} \ln \frac{n_1}{n_2} = \frac{kT}{e} \ln \frac{n_2 + \Delta n}{n_2}$. For $\Delta n \ll n_2$, the photovoltage is proportional to the exciting intensity. Such a photovoltage would be independent of the direction of uniformly absorbed illumination, as is observed.

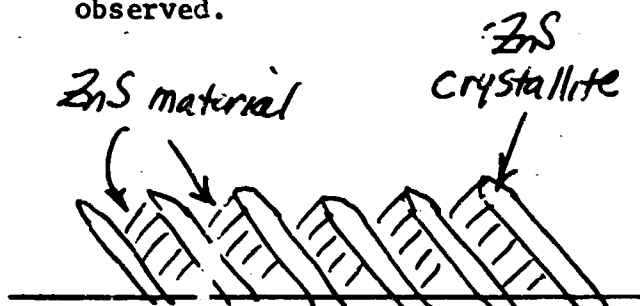


Fig. 1

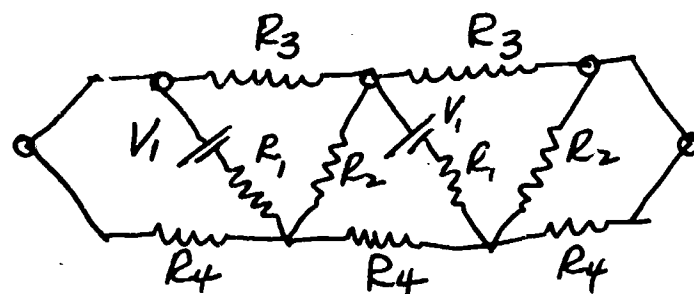


Fig. 2

To explain the addition of the photovoltages of the single crystals and the changes in resistance and in photovoltage under various conditions of illumination we approximate the sample by the circuit diagram shown in Fig. 2. R_1 and V_1 represent the resistance and photovoltage of each single crystal, while R_2 , R_3 and R_4 represent the interspersed and surface material between the single aligned crystals. It is quite obvious that this equivalent circuit is only a rough approximation of the actual situation, but it enables one to understand the experimental results obtained. If there is any crystal alignment in the direction of R_1 , the photovoltages of the single crystals (V_1) will be put in series to each other and the total photovoltage of the layer will be a partial addition of the single photovoltages as long as R_2 does not exhibit a counter

photovoltage of the same magnitude as that of R_1 .

We assume that R_1 shows a strong photoconductive response, R_2 shows only a weak one, and R_3 and R_4 show a noticeable response only with strongly absorbed light, otherwise their resistance is even greater than R_1 and R_2 .

In the dark, the sample resistance is given by $k(R_1 + R_2)$ where k is the number of crystallites. When the sample is illuminated by homogeneously absorbed light ($\lambda > 3400\text{\AA}$), R_1 becomes appreciably less than R_2 so that the sample resistance decreases to kR_2 . At the same time, a photovoltage appears which is the sum of the crystallite photovoltages (kV_1). An increase in intensity results in a linear increase in photovoltage (as long as $n_1 \ll n_2$) but with no increase in photoconductivity since R_2 is not as photoconductive as R_1 .

When short wave length illumination ($\lambda < 3400\text{\AA}$) is incident on the exposed surface, the density of excitation is very high in a thin surface layer; thus R_3 decreases markedly and may become lower than R_2 . This decreases the sample resistance as well as the photovoltage, since, with decreasing R_3 , photovoltaic elements become parallel to each other. A similar effect would occur if short wavelength illumination penetrated the substrate and was incident on the bottom surface.

It should be noted that one can also account for the decrease in photovoltage with short wavelength illumination if one assumes that the ZnS material between the aligned crystallites exhibits a photovoltaic

effect but in the opposite direction, because the electron concentration in R_2 has a gradient opposite to that of R_1 . This effect, however, is only observable at higher excitation densities, because of the smaller photoresponse of R_2 . Thus this model gives a complete description of the observations.

The main assumption in our model is that the interspersed material R_2 behaves differently than the single crystals R_1 . But this will occur when this material consists of a conglomeration of crystals and not of single crystals.

Table I

| <u>θ</u> | <u>R_{dark} (Ohms)</u> | <u>V_E (Volts)</u> | <u>V_O (Volts)</u> |
|----------------------------|--------------------------------------------|---------------------------------|---------------------------------|
| 0° | 2.2×10^{12} | 0 | 0 |
| 10° | 1.7×10^{13} | .190 | 20 |
| 20° | 1.3×10^{13} | .300 | 33 |
| 30° | 1.3×10^{14} | .360 | 150 |
| 40° | 1.8×10^{14} | .500 | 250 |

Table II

| <u>Tungsten Light Intensity</u> | <u>V_E(Volts)</u> | <u>V_O(Volts)</u> | <u>V_O/V_E</u> | <u>R</u> |
|-------------------------------------|-----------------------------|-----------------------------|------------------------------------|---------------------------|
| 10% | .044 | 23 | 520 | 5.2×10^{13} ohms |
| 25% | .125 | 65 | 520 | 5.2×10^{13} " |
| 40% | .190 | 95 | 500 | 5.0×10^{13} " |
| 60% | .300 | 150 | 500 | 5.0×10^{13} " |
| 80% | .400 | 200 | 500 | 5.0×10^{13} " |
| FULL | .500 | 250 | 500 | 5.0×10^{13} " |

Table III

| | <u>Tungsten Light</u> | <u>U.V. Light</u> | <u>U.V. + Tungsten</u> |
|-------------------------|-----------------------|----------------------|------------------------|
| V_e (Volts) | .780 | .22 | 1.0 |
| V_o (Volts) | 250 | 5.2 | 22 |
| V_o/V_e | 320 | 24 | 22 |
| R (ohms), calculated | 3.2 | 2.4×10^{12} | 2.2×10^{12} |

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Part III. INFRARED QUENCHING OF LUMINESCENCE IN ZNS PHOSPHORS ☆

To determine the spectral dependence of the infrared quenching of the ZnS phosphors prepared in this laboratory, the following experiments were performed.

The phosphor was excited by a high pressure mercury arc, and using appropriate filters, only the 3660\AA line was transmitted. In addition, the sample was exposed to infrared light from a Bausch and Lomb monochromator. The monochromator scanned the wavelength range from 6000\AA to $14,000\text{\AA}$ automatically; the IR intensity did not vary strongly over this range. A photomultiplier measured the luminescence output, and this signal was fed to a Leeds and Northrup Speedomax Recorder. Quenching would thus be observed as a diminution of the recorder deflection.

Measurements were made at both room temperature (RT) and liquid nitrogen temperature (LNT) on a large number of phosphors and Tables I, II, III give these results. Column 1 gives the sample number and Columns 2 through 5 give the firing conditions, gas and activation. Column 6 gives the relative emission intensity (without infrared) I and is corrected for the fact that the emission ranges from blue to red. Column 7 gives the wavelength at which the emission is maximum λ . When there are two emission maxima the second is also given with the

☆ Part of this work was reported at the International Symposium on Luminescence, Munich 1965.

percentage of the maximum. λ_1 and λ_2 refer to the two infrared quenching maxima (Columns 8,9) and λ_m gives the quenching minimum (when observed), Column 10. Columns 11 through 15 contain the same data for low temperature measurements. For easier analysis this table has been divided into three parts: Table I gives the data for self-activated phosphors, Table II for Cu activated phosphors, and Table III for phosphors with additional or different activation.

I. Self-activated Phosphor

The six phosphors in this table were fired using no activator but with varying amounts of Cl. The emission wavelength for all (at both RT and LNT) peaks at about 5000\AA , the so called "sky blue emission." In every case but number 123, the emission is considerably larger at LNT than at RT, probably due to thermal quenching at these temperatures. The largest emission is obtained when no Cl is added (number 134, fired at 1150°C with N_2); the next highest has $10^{-3}\%$ Cl and was fired at 1150°C with N_2 and O_2 . The weakest has $10^{-1}\%$ Cl and was fired with N_2 and O_2 at 1150°C . One can conclude that very little coactivator (Cl) is required for a "good" self-activated phosphor; a large amount of Cl seems to act as a "killer." The emission intensities of these phosphors are, as expected, smaller than those of the activated phosphors.

The infrared response of these phosphors falls into a marked pattern. At RT, there is the usual IR response found with many ZnS phosphors, and showing 2 distinct maxima; one at about 8000\AA ; the other at $13,000\text{\AA}$.

At low temperature, however, only one maxima, at about $10,000\text{\AA}$ is observed. This is quite unusual as regards IR behavior, and indicates that the mechanism of IR absorption by the activator changes at LNT. However, it should be noted that in these experiments only the decrease of equilibrium intensity due to the addition of IR is measured. This may not correspond to the actual response of the phosphor to IR as was observed in a ZnS:Cu,Cl phosphor prepared in this laboratory.¹

II. Cu-activated Phosphors

Table II lists the results for the Cu,Cl activated ZnS phosphors. At RT, all but one (number 125, much Cu, less Cl) show the typical green copper emission at about 5300\AA . At LNT a number of additional bands are observed. One of the most intense emitters (number 126) shows a maximum close to the self-activated peak in addition to the copper blue band (about 4500\AA). Number 124 also shows this effect. For these phosphors it is amazing that the copper green band decreases so much at LNT and that a definite maximum occurs at 5100\AA , the "self-activated band." All the others show either the copper green band or both the copper green and the copper blue bands. The emission intensity for every one of these samples is higher at LNT than RT. In the case of very high Cu concentration (1%) the ratio between LNT and RT emission intensity is extremely high indicating that phosphors with heavy Cu concentration already show very strong temperature quenching at room temperature.

The infrared response for two of these phosphors (number 126, 127) is normal: two maxima at RT but the long wavelength maxima disappearing at LNT~ (The stimulation response, however, shows this maximum, so that the disappearance in luminescence quenching does not indicate there is no IR response at these long wavelengths). Two other phosphors (numbers 124, 131) show only the short wave length quenching maxima at both RT and LNT. The only phosphor prepared in both an N_2 and O_2 atmosphere (number 140) shows both maxima at RT and Lnt. This phosphor shows a considerably decreased fluorescent response which indicates that many non-radiative transitions occur. This may also be the cause of the long wavelength maximum at both RT and LNT. Phosphor number 125 shows the usual response at LNT: the emission is too weak to make meaningful measurements at RT.

In Table III the results obtained with phosphors with other activators are presented. The first two phosphors are Cu activated, with Al rather than Cl introduced as coactivator. At RT, both show the Cu green band, while phosphor number 215 (lower concentration) shows the Cu green band and a small amount of the Cu blue band. The latter phosphor shows the normal IR behavior at RT; at LNT both maxima are observed. Again, as indicated by its low emission, this shows many non-radiative transitions at LNT. Phosphor 213 shows a quenching only at the short wavelength region of the IR.

Phosphors 259 and 256 are activated with gold (coactivator Cl) and show only a weak luminescence (shifted to the yellow) at both RT and LNT. At LNT an additional blue band appears.

Phosphors number 106, 108 and 93 are all silver activated phosphors, with Cl as coactivator. The luminescence is in the blue, except for phosphor number 93 which shows some Cu green luminescence at both RT and LNT. This indicates, for this phosphor at least, that some Cu has been accidentally incorporated.

These three phosphors show the same IR response as the self-activated phosphors in Table 1. At RT, the quenching follows the usual pattern of a short and long wavelength maxima ($\sim 0.8\mu$ and 1.3μ). At LNT there is only one maxima- at about 1.0μ . Thus, these two groups of phosphors (self-activated and Ag) show a quite different maximum at LNT than obtained at RT, whereas with the Cu activated phosphors, one of the two peaks seen at RT disappears at LNT, but the other remains. The fact that a new maximum appears is quite unusual, and as pointed out above, may be due to the fact that the decrease in luminescence may not describe the true IR response.

The remaining phosphor was activated with Cu, Cl and Cr; the latter gives rise to a photosensitive EPR signal resulting from electrons trapped in deep-lying levels due to Cr^{+} .⁽²⁾ The infrared response is the usual one found in Cu activated phosphors (two bands at RT), but instead of the long wavelength band disappearing it is quite noticeable at LNT. This is probably due to the increased quenching of this phosphor so that a decrease is observed even at LNT.

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TABLE I.

| 1. SAMPLE # | 2. FIRING CONDITIONS GAS; TEMP. | 3. ACTIVATION | | | 6. ROOM TEMPERATURE | | | 9. LIQUID NITROGEN TEMPERATURE | | | 12. LIQUID NITROGEN TEMPERATURE | | | 15. LIQUID NITROGEN TEMPERATURE | | |
|----------------|----------------------------------------|------------------|------|---------|---------------------|------|-------------------------------------|-------------------------------------|-------------------------------------|-----|---------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|---|---|
| | | % Cl | % Cu | % OTHER | I | E | $\lambda_1 \times 10^3 \text{ \AA}$ | $\lambda_2 \times 10^3 \text{ \AA}$ | $\lambda_m \times 10^3 \text{ \AA}$ | I | E | $\lambda_1 \times 10^3 \text{ \AA}$ | $\lambda_2 \times 10^3 \text{ \AA}$ | $\lambda_m \times 10^3 \text{ \AA}$ | I | E |
| 134 | N ₂ ; 1150°C | 0 | 0 | 0 | 9 | 5000 | 8.4 | 13.2 | 11.2 | 125 | 5000 | 10.2 | — | — | — | — |
| 123 | N ₂ ; 1150°C | 10 ⁻³ | 0 | 0 | 19 | 5000 | 8.4 | 13.4 | 10.8 | 9 | 4800 | — | — | — | — | — |
| 202 | H ₂ S; 1150°C | 10 ⁻³ | 0 | 0 | 3 | — | 8.4 | 13.4 | 11.0 | 20 | 5000 | 10.4 | — | — | — | — |
| 180 | N ₂ ; 880°C | 10 ⁻³ | 0 | 0 | 2 | 5000 | 7.6 | 13.4 | 11.2 | 5 | 4950 | 10.0 | — | — | — | — |
| 143 | N ₂ O ₂ ; 1150°C | 10 ⁻³ | 0 | 0 | 7 | 5000 | — | — | — | 50 | 5000 | 9.6 | — | — | — | — |
| 144 | N ₂ O ₂ ; 1150°C | 10 ⁻¹ | 0 | 0 | 0.6 | 5050 | 8.6 | 13.2 | — | 11 | 5000 | 10.0 | — | — | — | — |

TABLE II.

| 1. SAMPLE # | 2. FIRING CONDITIONS GAS; TEMP. | 3. ACTIVATION | | | 6. ROOM TEMPERATURE | | | 9. LIQUID NITROGEN TEMPERATURE | | | 12. LIQUID NITROGEN TEMPERATURE | | | 15. LIQUID NITROGEN TEMPERATURE | | |
|----------------|----------------------------------------|------------------|----------------------|---------|---------------------|------|-------------------------------------|-------------------------------------|-------------------------------------|-----|---------------------------------|-------------------------------------|-------------------------------------|-------------------------------------|---|---|
| | | % Cl | % Cu | % OTHER | I | E | $\lambda_1 \times 10^3 \text{ \AA}$ | $\lambda_2 \times 10^3 \text{ \AA}$ | $\lambda_m \times 10^3 \text{ \AA}$ | I | E | $\lambda_1 \times 10^3 \text{ \AA}$ | $\lambda_2 \times 10^3 \text{ \AA}$ | $\lambda_m \times 10^3 \text{ \AA}$ | I | E |
| 127 | N ₂ ; 1150°C | 10 ⁻¹ | 5 × 10 ⁻³ | 0 | 140 | 5350 | 8.6 | 13.4 | 10.8 | 200 | 5350 | 8.0 | — | — | — | — |
| 126 | N ₂ ; 1150°C | 10 ⁻¹ | 5 × 10 ⁻² | 0 | 340 | 5250 | 7.6 | 12.0 | 11.0 | 420 | 5100 4950(30) | 8.0 | — | — | — | — |
| 124 | N ₂ ; 1150°C | 10 ⁻¹ | 10 ⁻¹ | 0 | 150 | 5300 | 7.8 | — | — | 300 | 5100 4600(55) | 8.0 | — | — | — | — |
| 131 | N ₂ ; 1150°C | 1 | 5 × 10 ⁻² | 0 | 200 | 5250 | 8.0 | — | — | 310 | 5320 4600(32) | 7.8 | — | — | — | — |
| 140 | N ₂ O ₂ ; 1150°C | 10 ⁻¹ | 5 × 10 ⁻² | 0 | 38 | 5400 | 7.6 | 13.2 | 11.2 | 44 | 5350 4650(8) | 7.8 | 13.6 | 12.4 | — | — |
| 125 | N ₂ ; 1150°C | 10 ⁻¹ | 1 | 0 | 1 | 5830 | — | — | — | 150 | 5350 | 7.4 | — | — | — | — |
| 129 | N ₂ ; 1150°C | 1 | 1 | 0 | 10 | 5400 | ~8.0 | — | — | 420 | 5270 | 7.6 | — | — | — | — |

